

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICANT: DAVID HUGHES HORNE
SERIAL NO.: 10/809,989
FILED: March 26, 2004
FOR: PROCESS FOR INCREASING STRENGTH, FLEXIBILITY AND
FATIGUE LIFE OF METALS
GROUP ART UNIT: 1765
EXAMINER: ANITA KAREN ALANKO

AFFIDAVIT

STATE OF UTAH)
 : ss
COUNTY OF SALT LAKE)

Comes now David Hughes Horne, the inventor of the above-entitled invention for the application identified in Serial No. 10/809,989, and responds as follows:

Response to USPTO Office action on Application No. 10/809,989 for Applicant HORNE, DAVID HUGHES (US Application No. 2005/0082259) in Art Unit 1765 by Anita K. Alanko.

1. Under "Specification" in the Referenced Office Action, page 2 to correct the case of tradenamed products and a grammatical error:
 - (a) As noted by the examiner, request that the trademark or tradename "SUPER CORR B" noted in TABLE II on page 3 be amended to read "SUPER CORR A or B in upper case letters.

Reasons for Change: The Environmental Protection Agency has prohibited the manufacture of HCFC 141b solvent (with possible exceptions) which was in SUPER

CORR B so it no longer is made in the United States. SUPER CORR A is the replacement product which Battelle testing has shown is as effective to prevent corrosion as the SUPER CORR B. However, there still is some SUPER CORR B in existence which the EPA allows to be used for aircraft servicing. In addition, LektroTech has moved, but a new telephone number for the marketing manager is “(813) 390-7800.”

(b) A second CPC vendor noted in TABLE II is the International Lubricants and Fuel Consultants (ILFC), Rio Rancho, NM which manufactures a product called “1006 CON-TAC” that in the Application was written in mixed, upper and lower, case, also. Their product, too, should be in upper case only.

(c) On page 3, Paragraph [0020], line 20 beginning with “. . . elevating the temperature to 200°F. at . . .” delete the word “at.”

2. Under “Claim Rejections – 35 U.S.C. 112” by the examiner (Referenced Office Action, page 2):

(a) The examiner stated, “Claims 2-3 are rejected under 35 U.S.C. 112, first paragraph, because the specification, while being enabling for using SUPER CORR B, does not reasonably provide enablement for any corrosion preventive compound.” Skipping a sentence the examiner also wrote, “The specification enables the use of SUPER CORR B as a corrosion preventive compound, but does not enable the use of any corrosion preventive compound.

Response: Table II on page 3 of the Application in which SUPER CORR B is mentioned also mentions The International Lubricant and Fuels Consultants’ product 1006 CON-TAC (which should be in upper case, too). The following explains why not just any

product labeled as a corrosion preventive compound should be considered acceptable for the use of this technology.

Beginning in 1990 extensive laboratory and field corrosion testing of gold-plated electrical connector contacts and 1010 steel test-plates performed by Battelle Columbus for the US Air Force was reported at the IEEE Hulm Conference in 1996 by Battelle's principle investigator, Dr. William H. Abbott¹. Abbott revealed that of twelve prominent products being purchased by the DOD that were touted to be corrosion preventive compounds (CPCs), four actually accelerated corrosion in some tests, six products had some corrosion inhibiting ability, but only two were deemed excellent corrosion inhibitors or truly corrosion preventive compounds (CPCs) in laboratory salt spray tests and in long term, two year, outdoor tests at 10 field sites. Battelle's principal scientist for the study called the five companies that were selling the "corrosive CPCs" and asked what testing they had done that demonstrated their product's corrosion preventive abilities, and none of those companies had done any testing to see if their product truly prevented corrosion. But three of the four corrosive products claimed to be CPCs were qualified products for MIL-C-81309. One of the two which was considered as an excellent CPC in Battelle tests was not recommended in TABLE II of the patent application, because the flash point of that CPC spray was lower than zero-degrees Fahrenheit (a potential flame thrower). The Sandia Labs did the corrosion preventive testing on the 1006 CON-TAC.

This testing does not mean these could be the only effective CPCs. Indeed, the Specification Paragraph [0019] expressly states, "The two preferred products presented in Table II used in the testing are known to be excellent corrosion preventive compounds.

¹ Metals Handbook Ninth Edition, Vol. 5, Pg. 434, American Society of Metals, International, Metals Park, OH

They conform to MIL-L-87177A, and any CPC to be considered for use that conforms to MIL-L-87177A (or later revision), Grade A or B probably will provide the corrosion resistance to achieve optimum results from the invention but are not considered limiting of the invention.” The Grade A is an improved formula developed on a USAF testing contract to identify the SUPER CORR B base material with a more environmentally friendly solvent.

The Summary of the Invention, [0014], states after cleaning, etching, rinsing and drying the metal surface, “. . . coating the surface with a water displacing, low surface tension corrosion preventive compound” which could describe several if not many commercial corrosion preventive compounds.

Also, in paragraph [0018], the application of the CPC and its desired characteristic parameters are expanded to include a low surface tension (preferably less than 30-dynes/cm), a wide liquid temperature range to assure a perpetual liquid state, a low vapor pressure to prevent evaporation from the treated surface to at least 300°F, and very low water miscibility.” Paragraph [0018] concludes, “Table II lists some recommended CPCs for most metals.”

Thus, of the hundreds of products on the market claimed to be corrosion preventive compounds some really are not true CPCs, but there may be others that could qualify.

(b) Also under “Claim Rejections – 35 U.S.C. § 112 the second sentence after quoting the Code and stating “Claims 2-3 are rejected . . .” the Office Action reads, “The specification does not enable any person skilled in the art to which it

pertains, or with which it is most nearly connected, to make and use the invention commensurate in scope with these claims.”

Response: The specification documents the procedures beginning in paragraph [0014] and continuing with [0015], [0016], [0017], [0018], and [0019] which provide substantial detail to enable a person skilled in the art of metalworking and to make and use the process.

On page three of the Office Action, the examiner rejected claims 1-3 as being indefinite citing several words in the text as relative terms. It is agreed that some of the terms are indefinite, so the claims are amended, however a few of the terms are used normally in the art.

The first of these words is “minimizing,” which is used in the context as reducing something to a reasonably acceptable level for the expected environment considering the ability of the technical art, the costs, and impacts of failure. Minimizing is understood by metals and corrosion control artisans as equivalent to “prevention” (if absolute prevention were possible for even some defined time) in contrast with the conditions or service life expected of untreated metal.

Examples of the use of the word “minimizing” by those expert in this art are in a chapter of the American Society of Metals (ASM International) Handbook Volume 13A, Corrosion: Fundamentals Testing, Protection, 2003 “Designing to Minimize Corrosion,” pp. 929-939. Minimizing corrosion is used in context as the editor of this section of the book stated, “Design can never be absolute, often decisions are a compromise based on cost and availability of materials and resources” (pg. 929). *See Attachment A.*

The examiner also noted the word “mitigate” as an indefinite word like “minimize” which also is understood by the artisans in the metals art reducing some condition in comparison

with untreated or unprotected metal by doing the best one can do under the circumstances.

Mitigate also is used in the ASM Handbook, pp 245-246 and 295-296. See Attachment B.

Subscribed and sworn to before me this 26th day of May, 2006.

David Hughes Horne
David Hughes Horne

Robert M. Kelly
Notary Public
Residing in Salt Lake City, Utah



NOTARY PUBLIC
ROBERTA M. KELLY
170 South Main, Ste 1500
Salt Lake City UT 84101
My Commission Expires Feb. 1, 2007
State of Utah

Designing to Minimize Corrosion

Peter Elliott, Corrosion and Materials Consultancy, Inc.

UNEXPECTED and frequently costly failures occur without sound and reliable engineering design, which includes the effective and correct choice of materials and the economic use of efficient controls and monitoring measures. Fine details of engineering design may be missed because of poor communication channels, sometimes compounded by human errors and a lack of proper care and attention. Unexpected premature failures can be harmful to personnel and adjacent equipment or parts. On occasion, a poor design can cause premature failure of even the most advanced corrosion-resistant materials.

Design Considerations

Design can never be absolute; often, decisions are a compromise based on cost and availability of materials and resources. Designing for corrosion control can only be effective if it is part of the overall design philosophy.

There are numerous textbooks, handbooks, and articles on corrosion; several offer choices for specific materials/environment systems (Ref 1-17). These reference sources provide a useful starting point for selecting materials, but a designer is seldom a corrosion engineer, so it is necessary to further convey essential corrosion knowledge to designers (Ref 18-27). Unlike conventional engineering, the basic difficulty is that corrosion is not a tangible property; it is more a behavioral pattern. Thus, to realize safe, reliable designs, it is essential that there be a rigid control on materials and fabrication and an extensive effort to eliminate human errors or misunderstandings that result from poor communication.

The results of a survey of chemical-processing plants (Ref 28) showed that design faults ranked highest (58%) in the reasons for failure. Of almost equal ranking was the incorrect application of protective treatments (55%), followed by categories that demonstrate a lack of knowledge about the operating conditions (52%), lack of process control (35%), and an unawareness that there was actually a corrosion risk (25%).

In an ideal world, designers would call for some corrosion assessment prior to preparing the detailed engineering design. Typically, schemes would permit some form of evaluation with re-

spect to both function and the necessary action, for example, from the proposal-to-production planning stages (Fig. 1) (Ref 28). In the practical, real world, however, communication of agreed reasons for failures may not always reach the designer. Indeed, communication to contractors, who are closest to the application, is even poorer (Ref 28, 29). Studies have shown that, while management is always informed of the reasons for failure in the chemical-processing industry, site personnel are informed only 77% of the time; designers, 55%; materials suppliers, 37%; and contractors, only 11% of the time.

Drafter's Delusions. A further complication in designing against corrosion relates to the general interpretation of design drawings in what has been referred to as drafter's delusions. For example, the drafter might be considering a certain piece of equipment without knowledge of the fact that there may be unusual shapes, moving parts, or environmental issues. A lack of attention to design detail causes many premature failures by corrosion-related processes. All too often, the designer will have in mind one thing, which, in reality, becomes totally different. For example, a simple crossover line between two reactor vessels might, in practice, become an extended line with several turns, merely to position a shutoff valve at a more convenient and accessible position closer to ground level. There are countless examples of this situation in real-world failure analysis, where the actual designs were not those originally intended (Ref 29-35); further examples are provided in the following pages.

Quality assurance and control usually ensure that the requested material is what it should be and that it was inspected and tested as specified. However, materials controls at fabrication are sometimes less than perfect. In one case, an inspector noticed a blemish on the outside of a steel pressure vessel. On closer scrutiny (from the vessel interior), the problem was found to be a steel bolt that had been inadvertently rolled into the steel plate during fabrication (Fig. 2).

While considering materials, it is important to avoid nonspecific descriptions or terms in reference to design drawings and specifications. There are many instances where generic terms, such as *stainless steel*, *bronze*, *Hastelloy*, or *Inconel*, are too vague, and the ultimate choice is

far from what was expected and required. Wherever possible, and notably, in high-risk areas, materials should be selected and tested according to code requirements (Ref 7, 36). Substitutes, if requested, should be properly evaluated before use.

Reliability Engineering. The designer should play a significant role in reliability management. The communication chain, or the reliability loop, from the designer, to the manufacturer, then to the user, and back to the designer is a key factor (Ref 29, 37). When a risk is well documented, it should be possible to overdesign or at least isolate the area to minimize risk to users. Where a risk of failure is high, the emphasis should be toward a fail-safe or no-fail/replace procedure. Failures vary considerably; the design function can be partially or totally affected, or the onset of failure can be gradual or sudden. The combination of sudden and total failure represents the worst catastrophic situation (e.g., explosions, fires, and total structural collapse), many of which can be attributed to a small design detail.

Corrosion Awareness

This article is intended to improve corrosion awareness, but clearly, this is only a starting point. To be effective, the user must also be willing to take action, and the designer should insist on appropriate codes and/or recommended working practices. Whether the necessary action will be taken is affected by financial, technical, safety, social, and/or political issues (Ref 37).

To prevent corrosion/degradation, the designer can:

- Avoid obvious design weaknesses (see subsequent examples)
- Use more reliable materials, even if this entails greater cost
- Introduce additional precautions, such as monitoring (Ref 38), inhibitors, cathodic protection, and coatings (Ref 39, 40)
- Establish efficient maintenance/repair teams having detailed procedures and including qualified surveyors, inspectors, and supervisors
- Ensure that standby products are available, fully labeled, and properly stored (using desiccants and noncorrosive packaging)

ASM Handbook®

Volume 13A Corrosion: Fundamentals, Testing, and Protection

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Charles Moosbrugger, Project Editor

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Nancy Hrivnak, Jill Kinson, and Carol Polakowski, Production Editors

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Beverly Musgrove



Materials Park, Ohio 44073-0002
www.asminternational.org

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form metal hydroxides and H^+ ions. For charge neutrality, anions such as chloride then migrate to the site from the bulk solution. Because of the geometry of the site, these ions become trapped and result in increasing concentration and higher rates of dissolution of the alloy. Therefore, the solution within pits and crevices tends to be acidic and highly concentrated.

In contrast, the lap-joint environment becomes neither concentrated nor acidic. This difference is due to the lack of an external cathodic reaction. In traditional pits and crevices, the majority of the cathodic reaction (e.g., $2O_2 + 2H_2O + 4e^- = 4OH^-$) occurs well away from the corrosion site. However, in lap-joint corrosion, the external surface often dries significantly before the occluded region (Ref 6). The lack of electrolyte on the external surface forces the cathodic reaction to occur within the occluded region. The production of OH^- ions in the cathodic reaction competes with the formation of H^+ ions in metal hydrolysis, and the result is a mildly alkaline environment in the case of aluminum (Ref 32).

Example 4: Crevice Corrosion of Titanium Alloys. Titanium alloys are among the most resistant to crevice corrosion. Extensive studies of crevice corrosion of these alloys have shown that these alloys do not suffer from crevice corrosion at temperatures less than 70 °C (158 °F). Ikeda et al. (Ref 34) have shown that by alloying with small amounts of molybdenum, nickel, or palladium, resistance to crevice corrosion is maintained to almost 200 °C (392 °F) in 10 wt.% $FeCl_3$.

Testing

An excellent review of testing methods has been presented by Kearns (Ref 35). This section briefly reviews the types of methods that have been developed for differentiating and ranking the resistance of alloys toward crevice corrosion. See also the article "Evaluating Crevice Corrosion" in this Volume.

Standardized Accelerated Tests. A variety of ASTM standards have been developed in which materials are exposed to severe environments for crevice corrosion. For example, the ferric chloride test (Ref 36) employs a high concentration of chloride at a low pH, with the ferric/ferrous ion couple providing an elevated potential. Increased temperature can also be used to accelerate the process.

To further exacerbate the situation, tight crevices can be imposed by using a multiple-crevice assembly (Ref 37) as shown in Fig. 8. The castellated washer provides up to 20 possible sites for crevice corrosion on each side of the coupon. By applying a consistent torque, several replicate samples can be used to develop a statistical basis for comparison of alloy resistance.

Electrochemical Testing. There are a number of tests that combine electrochemical polarization with elevated temperature to determine the critical crevice temperature (CCT). The CCT can

then be used to rank the relative crevice-corrosion resistance. Typically, a constant positive potential is applied while a programmed temperature change is imposed. The current necessary to maintain the constant potential is monitored. When the applied potential and temperature combination is sufficient to cause crevice corrosion, the applied current increases dramatically and the CCT is thus determined. It has been found that this transition from passive to crevice corrosion is very sharp and reproducible (Ref 38).

Sridhar and coworkers (Ref 39) followed the work of Tsujikawa and Hisamatsu (Ref 40) by using a modification of ASTM F 746 (Ref 41) to determine the repassivation potential for crevice corrosion. In their approach, crevice corrosion is initiated under controlled conditions using a high applied potential. The ability of the material to resist localized corrosion is quantified by determining the highest applied potential at which the material can repassivate. They have shown that the repassivation potential determined in this way is an excellent measure of the long-term performance of stainless and nickel-base alloys as shown in Fig. 9 (Ref 39). They have demonstrated that a properly measured repassivation potential can be used as an engineering design criterion, not just as a comparative screening parameter. By maintaining the open-circuit potential of the surface of a material below the repassivation potential, significant localized corrosion is completely prevented. Although it has not been proved that absolutely no crevice corrosion initiates, propagation is stifled to the point of insignificance on a large engineering structure. This demonstration provides

not only a valuable tool for preliminary design, but also a criterion to ensure that localized corrosion has been stopped once started.

Prevention or Mitigation of Crevice Corrosion

Strategies for the prevention of crevice corrosion or lessening its effects include design awareness, use of inhibitors, and electrochemical control methods.

Design. The primary means of preventing crevice corrosion is careful design. To the extent possible, passive materials should not be placed in crevice arrangements. Unfortunately, in most engineering structures complete avoidance of crevices is not practical; pipe sections must be connected via flanges, vessels are not made from a single sheet of material, and so forth. In these cases, careful design would dictate maximizing the gap and minimizing the length (depth) of any crevices created. By making the geometry less restricted, the development of an aggressive chemistry is more difficult, and the potential drop within the crevice will also be smaller.

Making a crevice so tight as to preclude electrolyte uptake is usually not practical in the long term. Extremely tight crevices that are *not* watertight exhibit tremendous capillary action, drawing in solution over long distances just as a large tree draws moisture from the soil to the top of its canopy. The extremely restricted geometry is perfect for the development of severe crevice corrosion. Even crevices that are initially "too tight for water uptake" will likely loosen with time, leading to electrolyte ingress.

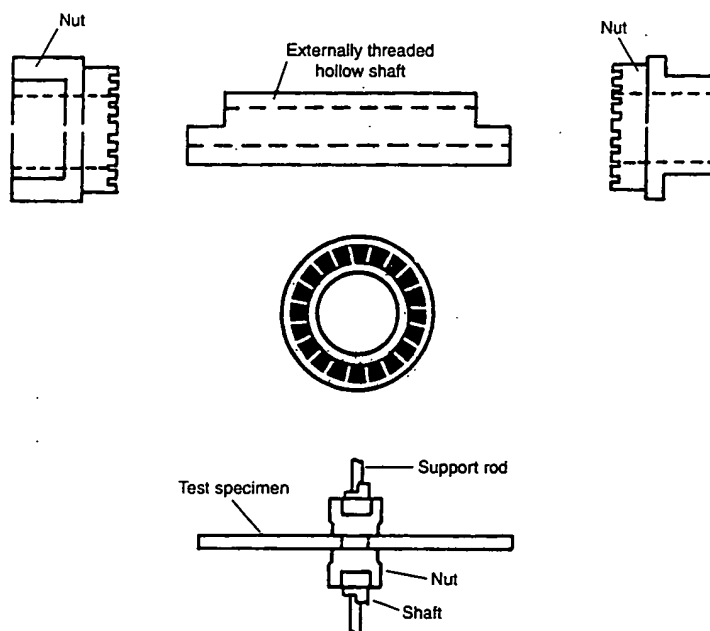


Fig. 8 Various views of the multiple-crevice assembly. Source: Ref 11

Alkire and coworkers (Ref 42) have demonstrated the effects of flow on the inhibition of pitting. Similar ideas can be applied to crevice corrosion. In both instances, flow would act to inhibit initiation of attack to the extent that the flow lines enter the occluded region. For pit initiation, flow at the surface is very successful at delaying or preventing aggressive solution development. In a crevice, the large length-to-gap ratio makes initiation control much less effective than for pits.

Ironically, once a crevice has initiated, the flow of solution across the fully exposed surface generally acts to increase the propagation rate. This effect results from the increased flow on cathodic reactions on the fully exposed surface that are mass-transport controlled, such as oxygen reduction. As the cathodic reaction rate increases, the polarization of the internal, crevice anode increases as well, leading to increased dissolution rates. This effect is mitigated to the extent that the crevice is under ohmic control due to the restricted geometry (Ref 43).

Material selection for crevice-corrosion resistance normally follows that used for pitting resistance. Ratings based on composition have been published for ferrous materials, using the CCT as the figure of merit. There is a strong correlation between the CCT and the pitting resistance equivalence number (PREN) for stainless steels, as might be expected. In both cases, the more chromium, molybdenum, and nitrogen in the alloy, the higher the resistance. Note that the CCT is always lower than the critical pitting

temperature (CPT). An example of this phenomenon (Fig. 10) shows the effect of alloyed molybdenum on the resistance of stainless steels.

In general, the lower the passive current density of the material, the smaller its active/passive transition, and the more stable its oxide, the more resistant it is to crevice corrosion. Of particular importance is the dependence of these parameters on the pH and chloride content.

Inhibitors. In addition to alloying, solution-phase inhibition has been shown to reduce the occurrence of crevice corrosion. Again, similarities to inhibitors for pitting have been observed, as expected. Inhibitors tend to be less effective for crevice corrosion than pitting because of the much longer transport lengths required for the inhibitor to move close to the active region. In order to arrive there in sufficient concentration to be effective, the bulk concentration generally needs to exceed the bulk chloride concentration by a factor of five or more (on a molar basis).

Many nonaggressive anions have been investigated as localized corrosion inhibitors in Cl^- solutions, including SO_4^{2-} , ClO_4^- , and NO_3^- (Ref 44). Anions that are not electroactive (e.g., SO_4^{2-} and ClO_4^-) have been suggested to function as inhibitors via a supporting electrolyte effect (Ref 45-47). A supporting electrolyte effect occurs when a species—for example, sulfate—competitively migrates and adsorbs on the metal surface with Cl^- , thereby slowing or preventing the increase in the Cl^- concentration in the occluded region. Thus, the relative concentration and mobility of the other anion compared to Cl^-

are critically important. The presence of SO_4^{2-} would delay the accumulation of Cl^- in the occluded site, but the same occluded-site chemistry would be necessary for initiation to occur. Newman and Ajjawi (Ref 48) proposed that some inhibiting anions form a salt film during the early stages of localized corrosion initiation, under which passivation can occur via inward water diffusion. In the case of NO_3^- , an electroactive anion, Newman et al. (Ref 48, 49) proposed that inhibition occurs via one of three possible mechanisms:

- Electroreduction of NO_3^- to NH_4^+ , which consumes H^+ and produces water
- Electroreduction of NO_3^- to elemental nitrogen, which in turn blocks some proportion of the active kink sites on the surface at which dissolution occurs
- Formation of a redox couple between Fe^{2+} and NO_3^- that consumes H^+ at low pH and assists in the formation of an Fe-OH barrier film at high pH

In the case of crevice corrosion, Lu and Ives (Ref 50) has shown that cerium treatments of fully exposed surface can inhibit crevice corrosion of stainless steels. This effect is presumably by a poisoning of the rate of oxygen reduction (cerium oxides are poor oxygen reduction surfaces), which leads to an inability of the external surface to support the dissolution rate of the occluded region to the extent necessary to produce and maintain an aggressive occluded solution. Insulating coatings (e.g., paints) on the fully exposed surface can also mitigate crevice corrosion in a similar manner by reducing the ability of that surface to consume the electrons generated by the anodic dissolution within the crevice. This decrease in cathode area limits the rates of anodic dissolution possible within the crevice and thereby can limit crevice corrosion. It should be noted that many corrosion-resistant alloys are notoriously difficult to paint due to poor adherence between the passive film and the organic coating. Loss of adhesion can lead to additional crevice sites.

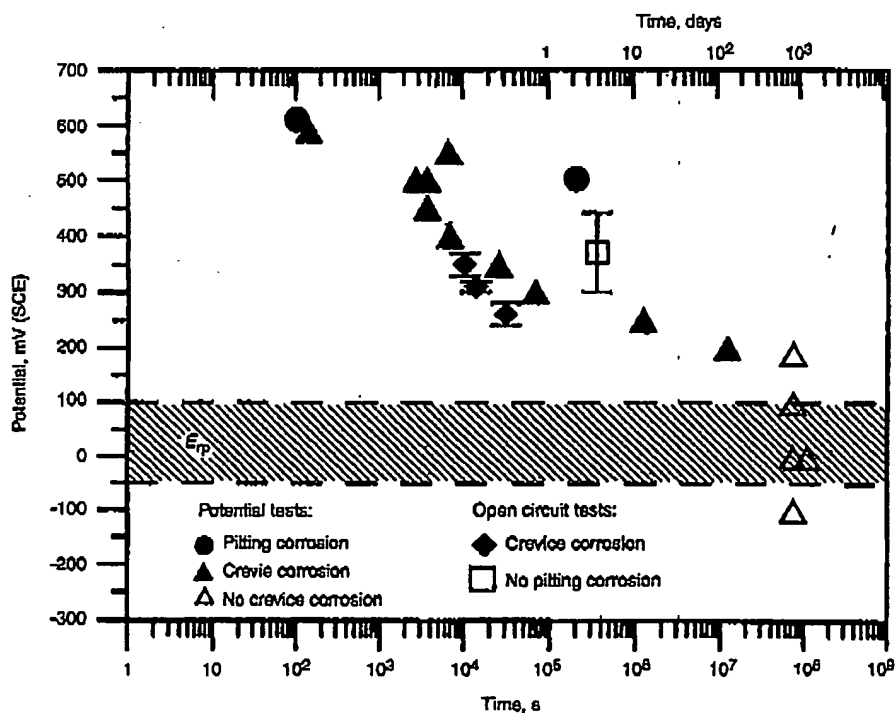


Fig. 9 Effects of applied potential and corrosion potential on the pitting- and crevice-corrosion initiation time for alloy 825 in 1000 ppm Cl^- at 95 °C (203 °F). Note that at and below the repassivation potential, E_p , no initiation occurs out to at least three years. Source: Ref 39

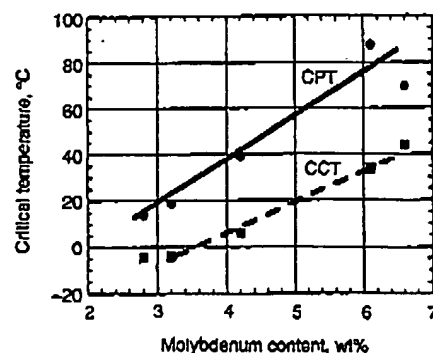


Fig. 10 Critical pitting and crevice temperatures (CPT and CCT, respectively) as a function of molybdenum content for commercial austenitic stainless steels. Source: Ref 35

susceptible. *Tramline corrosion* is a term applied to preferential HAZ corrosion concentrated at the fusion boundaries and has been observed in acidic aqueous environments such as acid mine waters.

There is clearly a microstructural dependence, and studies on HAZs show corrosion to be appreciably more severe when the material composition and welding parameters are such that hardened structures are formed. It has been known for many years that hardened steel may corrode more rapidly in acid conditions than fully tempered material, apparently because local microcathodes on the hardened surface stimulate the cathodic hydrogen evolution reaction. The rate of corrosion is usually governed by the cathodic (reduction) rate, when other limiting factors are not present, and therefore, it is a factor in acidic environments but less so in neutral or alkaline conditions. On this basis, it is proposed that water treatments ensuring alkaline conditions should be less likely to induce HAZ corrosion, but even at a pH near 8, hydrogen ion (H^+) reduction can account for approximately 20% of the total corrosion current; pH values substantially above this level would be needed to suppress the effect completely. Furthermore, if such treatments may be useful to control preferential HAZ corrosion when it has not been anticipated, it is considered to be more reliable to avoid the problem through design. Avoidance through selection of appropriate material or welding procedure, for example, to minimize hardness, is the preferred remedial approach, because postweld heat treatment (PWHT) may necessitate temperatures high enough for normalizing to gain full benefit, which is usually impractical (Ref 1).

In some oil and gas production environments, preferential weldment corrosion may lead to enhanced HAZ attack or weld metal corrosion. In the late 1980s, studies of the problems associated with preferential weldment corrosion in sweet oil and gas production systems were undertaken (Ref 5). In some cases, the HAZ was attacked, while in other cases, the weld metal was preferentially corroded. Where enhanced HAZ corrosion was observed, the composition was more influential than the microstructure; however, hardened transformed microstructures suffered increased corrosion. The postweld heat treatment at 590 °C (1100 °F) for stress relief was beneficial in reducing HAZ attack (Ref 2), despite the previous comments.

HAZ/Fusion Line Corrosion of Welded Line Pipe. There is a particular case of preferential weldment corrosion worth highlighting in respect to electric-resistance-welded/high-frequency-induction-welded (ERW/HFI) pipe, where attack of the seam weld HAZ/fusion line can occur in aqueous environments or when exposed to the water phase in a mixed-phase system due to flow conditions or water dropout at low points. This grooving corrosion has been attributed to inclusions within the pipe material being exposed at the pipe surface and modified by the weld thermal cycle (Ref 4). A normalizing

heat treatment can reduce or prevent occurrence. However, the major remedial action is the selection of a cleaner alloyed steel (Ref 6). Corrosion is due to electrochemical-potential differences (galvanic corrosion) between the HAZ/fusion line and the parent material, attributed to the unstable MnS inclusions produced during the welding cycle. It is highlighted that the potential difference may only be of the order of perhaps 30 to 70 mV, but the low surface area ratio of anode to cathode results in high corrosion rates (between 1 to 10 mm, or 0.04 to 0.4 in., per year). Mitigation against this form of corrosion was achieved through modified steel composition in the 1970s; the addition of copper plus reduced sulfur to minimize MnS formation and the addition of calcium, nickel, or titanium to stabilize the remaining sulfur eliminates the potential difference. Such corrosion has become less common in recent years, due to awareness of these issues and remedial measures.

Preferential Weld Metal Corrosion

The weld metal in a carbon-manganese steel may suffer preferential corrosion, but again, if quality corrosion mitigation is in place for the main structure, such as coating or cathodic protection, this preferential attack is also normally prevented. However, there are cases where coating failure or inefficient inhibition can then lead to localized corrosion.

It is probable that similar microstructural considerations also apply to the preferential corrosion of weld metal, but in this case, the situation is further complicated by the presence of deoxidation products, their type and number depending largely on the flux system employed. Consumable type plays a major role in determining weld metal corrosion rate, and the highest rates of metal loss are normally associated with shielded metal arc electrodes using a basic coating. In seawater, for example, the corrosion rate for a weld made using a basic-flux-coated consumable may be three times as high as for weld metal from a rutile-flux-coated consumable. Fewer data are available for submerged arc weld metals, but it would appear that they are intermediate between basic and rutile flux shielded metal arc electrodes and that a corrosion rate above that of the base steel can be expected. In many cases, the underlying cause of the problem is the electrochemical potential difference between the weld metal and the adjacent parent steel, as discussed subsequently.

Galvanic Corrosion

Some of the earliest problems of weld metal corrosion related to ships in arctic waters, where the action of ice abraded the paint to expose bare steel and damaged the anodes, thus rendering the cathodic protection system ineffective. In these cases, it was observed that enhanced corrosion of the weld metal was due to electrochemical

potential differences between the weld metal and the base metal, such that the weld metal is anodic in the galvanic couple. Further detailed studies were undertaken in the late 1980s to assess more modern steels and welding consumables in arctic waters off Canada (Ref 7). Both HAZ and weld metal attack were observed, and the general conclusions were that for steels between 235 and 515 MPa (34 and 75 ksi) minimum yield strength, high manganese content (1.4%) in the parent steel resulted in enhanced preferential HAZ attack, but this could be reduced via increased heat input during welding. Generally, the rate of weld metal attack was dependent on the nickel and copper contents of the welding consumable and was less influenced by parent steel composition, although a steel with copper, nickel, and chromium additions led to a more noble parent steel, hence accelerating weld metal attack. It was noted that parent steel with low silicon content led to increased weld metal corrosion, supporting the earlier findings that silicon < 0.2% can be detrimental, but the opposite was observed for silicon in the weld metal.

It is highlighted that, as for the autogenous seam weld in ERW/HFI pipe, the difference in corrosion potential for the separated regions (parent steel, HAZ, and weld metal) may be only a few tens of millivolts, but due to the low surface area ratio of anode to cathode in conductive solutions, the attack on the anodic weld metal or HAZ may be very high. Also, on-going corrosion of the parent steel will continue, and if this rate is unacceptable, mitigation or protection methods are required for the base material in addition to consideration of ways to control the enhanced localized attack at the weldments. Generally, such weld metal attack has occurred in high-conductivity media, and the measures described to ensure the weld metal is cathodic (more noble) relative to the base metal have been successful. However, this may not be successful in different environmental conditions.

Mitigation of Preferential Weldment Corrosion

Optimized process selection and welding procedures will assist in achieving good-quality welds, ensuring full weld penetration and mini-

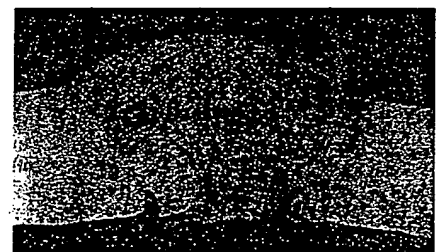


Fig. 1 Preferential corrosion in the heat affected zone of a carbon steel weldment after service in an aqueous environment. 5×. Source: Ref 3

mizing excessive weld reinforcement; postweld dressing by grinding (a costly method) can be effective in minimizing the geometric effects.

A stress-relieving heat treatment may be effective in reducing residual stress (internal weld shrinkage stress) and metal hardness to safe levels in most cases of concern regarding environmentally assisted cracking (stress-corrosion cracking and sulfide stress cracking).

A PWHT stress relief has also been reported to be beneficial in reducing HAZ attack (Ref 1). However, in other cases, avoidance through selection of appropriate material or welding procedure is the preferred remedial approach, because PWHT may necessitate temperatures high enough for normalizing to gain full benefit, which is usually impractical (Ref 1).

Mitigation of preferential weld metal corrosion may be achieved in some cases via alloying additions to make the weld metal cathodic to the adjacent base metal. It must be noted that although the weld becomes cathodic to the base material, accelerated corrosion of the base metal is unlikely, because the anode-to-cathode surface area ratio becomes very high. However, care is required in extrapolating remedial measures proven in one environment, because they may not be efficient in different conditions. For example, the factors influencing such localized corrosion in sweet oil and gas environments are complex, and the use of nickel-containing weld metal for the root, successful in mitigating attack in seawater injection systems, has led to incidents of preferential attack in particular systems operated at temperatures of approximately 70 to 80 °C (160 to 175 °F) (Ref 8).

However, when introducing measures to avoid weld metal corrosion, care must be taken to avoid enhanced corrosion of the adjacent HAZ, due again to galvanic effects, particularly where the environment has relatively low conductivity, such as freshwater (Ref 4).

In summary, preferential weldment corrosion of carbon steels has been observed in diverse applications, from plate steels in the marine industry to pipe and process equipment, piping

tankage, pressure vessels (Ref 9), and similar equipment in the oil and gas sectors. Some typical case histories are presented as follows, but mitigation in most cases requires an assessment of the particular environment and materials involved and will likely necessitate some testing to evaluate the performance in service.

Industrial Case Studies

In one case, premature weld failures were experienced in a 102 mm (4 in.) ASTM A53 pipe that was used to transfer a mixture of chlorinated hydrocarbons and water. During construction, the pipeline was fabricated with E7010-AI welding electrodes (see Table 1 for the compositions of all materials discussed in these examples). Initial weld failures and subsequent tests showed the following welding electrodes to be anodic to the A53, grade B, base metal: E7010-AI, E6010, E6013, E7010-G, and E8018-C2. Two nickel-base electrodes—Inco-Weld A (American Welding Society, or AWS, A5.11, class ENiCrFe-2) and Incoloy welding electrode 135—were tested; they were found to be cathodic to the base metal and to prevent rapid weld corrosion. The corrosion rates of these various galvanic couples are listed in Table 2.

Another example is the failure of low-carbon steel welds in seawater service at 25 °C (75 °F). Fabrications involving ASTM A285, grade C, plate welded with E6013 electrodes usually start to fail in the weld after 6 to 18 months in seawater service at this temperature. Welds made with E7010 electrodes do not fail. Tests were conducted in seawater at 50 °C (120 °F) using A285, grade C, plate welded with E6010, E7010-AI, and E7010-G. It was determined that E7010-AI was the best electrode to use in seawater and that E6010 and E7010-G were not acceptable (although they were much better than E6013), because they were both anodic to the base metal. A zero resistance ammeter was used to determine whether the electrodes were anodic or cathodic to the base metal.

In another case, welds made from E7010-AI electrodes to join ASTM A285, grade C, base metal were found to be anodic to the base metal when exposed to raw brine, an alkaline-chloride (pH > 14) stream, and raw river water at 50 °C (120 °F). When E7010-G was exposed to the same environment, it was anodic to the base metal in raw brine and raw river water and was cathodic to ASTM A285, grade C, in the alkaline-chloride stream. When the base metal was changed to ASTM A53, grade B, and A106, grade B, it was found that E7010-AI weld metal was cathodic to both when exposed to raw brine at 50 °C (120 °F).

Finally, routine inspection of a column in which a mixture of hydrocarbons was water washed at 90 °C (195 °F) revealed that E7016 welds used in the original fabrication were corroding more rapidly than the ASTM A285, grade C, base metal. Corroded welds were ground to sound metal, and E7010-AI was used to replace the metal that was removed. Approximately 3 years later, during another routine inspection, it was discovered that the E7010-AI welds were being selectively attacked. Tests were conducted that showed E7010-AI and E7016 weld metals to be anodic to A285, grade C, while E7018 and E8018-C2 would be cathodic. Corrosion rates of these various galvanic couples are given in Table 3.

These examples demonstrate the necessity for testing each galvanic couple in the environment for which it is intended. Higher-alloy filler met-

Table 1 Compositions of carbon steel base metals and some filler metals subject to galvanic corrosion. See Tables 2 and 3 for corrosion rates of galvanic couples.

Metal	Composition, wt %						
	C	Mn	Si	Cr	Ni	Fe	Others
Base metals							
ASTM A53, grade B	0.30	1.20	bal	...
ASTM A285, grade C	0.22	0.90	bal	...
Filler metals							
E6010	No specific chemical limits						
E6013							
E7010-AI	0.12	0.60	0.40	bal	0.4-0.65Mo
E7010-G	...	1.00(a)	0.80(a)	0.30(a)	0.50(a)	bal	0.2Mo, 0.1V
E7016	...	1.25(b)	0.90	0.20(b)	0.30(b)	bal	0.3Mo, 0.08V(b)
E7018	...	1.60(c)	0.75	0.20(c)	0.30(c)	bal	0.3Mo, 0.08V(c)
E8018-C2	0.12	1.20	0.80	...	2.0-2.75	bal	...
ENiCrFe-2 (Inco Weld A)	0.10	1.0-3.5	1.0	13.0-17.0	bal	12.0	1-3.5Mo, 0.5Cu, 0.5-3(Nb + Ta)
Incoloy welding electrode 135	0.08	1.23-2.50	0.75	26.5-30.5	35.0-40.0	bal	2.75-4.5Mo, 1-2.5Cu

(a) The weld deposit must contain only the minimum of one of these elements. (b) The total of these elements shall not exceed 1.50%. (c) The total of these elements shall not exceed 1.75%. Source: Ref 9

Table 2 Corrosion rates of galvanic couples of ASTM A53, grade B, base metal and various filler metals in a mixture of chlorinated hydrocarbons and water

The areas of the base metal and the deposited weld metal were equal.

Filler metal	Base metal corrosion rate		Filler metal corrosion rate	
	mm/yr	mils/yr	mm/yr	mils/yr
E6010	0.4	15	0.9	35
E6013	0.18	7	0.9	35
E7010-AI	1.3	50	4.3	169
E7010-G	1.7	68	2.8	112
E8018-C2	0.36	14	1.7	66
Inco Weld A	0.48	19	0.013	0.5
Incoloy welding electrode 135	0.36	14	<0.0025	<0.1

Source: Ref 9

Table 3 Corrosion rates of galvanic couples of ASTM A285, grade C, base metal and various filler metals at 90 °C (195 °F) in water used to wash a hydrocarbon stream

Filler metal	Base metal corrosion rate		Filler metal corrosion rate	
	mm/yr	mils/yr	mm/yr	mils/yr
E7010-AI	0.69	27	0.81	32
E7016	0.46	18	0.84	33
E7018	1.3	50	1.2	48
E8018-C2	2.2	85	1.04	41

Source: Ref 9